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An agency of Industry Canada

CA 2385802 A1 2003/11/09

(21) 2 385 802

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(22) Date de dépôt/Filing Date: 2002/05/09

(41) Mise à la disp. pub./Open to Public Insp.: 2003/11/09

(51) Cl.Int.^{7}/Int.Cl.^{7} D01F 9/12, B82B 3/00, C01B 31/02

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(54) Titre : METHODE ET APPAREIL DE PRODUCTION DE NANOTUBES DE CARBONE A PAROI SIMPLE

(54) Title: METHOD AND APPARATUS FOR PRODUCING SINGLE-WALL CARBON NANOTUBES

(57) Abrégé/Abstract:

The invention relates to a method for producing single-wall carbon nanotubes. The method of the invention comprises the steps of (a) providing a plasma torch having a plasma tube with a plasma-discharging end; (b) feeding an inert gas through the plasma tube to form a primary plasma; (c) contacting a carbon-containing substance and a metal catalyst with the primary plasma at the plasma-discharging end of the plasma tube, to form a secondary plasma containing atoms or molecules of carbon and atoms of the metal catalyst; and (d) condensing the atoms or molecules of carbon and the atoms of the metal catalyst to form single-wall carbon nanotubes. Alternatively, steps (b) and (c) can be carried out by feeding an inert gas and an inorganic metal catalyst through the plasma tube to form a primary plasma containing atoms of the inorganic metal catalyst and contacting a carbon-containing substance with the primary plasma at the plasma-discharging end of the plasma tube, to form a secondary plasma containing atoms or molecules of carbon and the atoms of metal catalyst. An apparatus for carrying out the method according to the invention is also disclosed.

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METHOD AND APPARATUS FOR PRODUCING SINGLE-WALL CARBON NANOTUBES

The present invention relates to improvements in the field of carbon nanotube production. More particularly, the invention relates to an improved method and apparatus for producing single-wall carbon nanotubes.

Carbon nanotubes are available either as multi-wall or single-wall nanotubes. Multi-wall carbon nanotubes have exceptional properties such as excellent electrical and thermal conductor, and are as strong as diamond. They have applications in numerous fields such as storage of hydrogen (C. Liu, Y.Y. Fan, M. Liu, H. T. Cong, H.M. Cheng, M.S. Dresselhaus, Science 286 (1999), 1127; M.S. Dresselhaus, K.A Williams, P.C. Eklund, MRS Bull. (1999), 45) or other gases, adsorption heat pumps, materials reinforcement or nanoelectronics (M. Menon, D. Srivastava, Phy. Rev. Lett. 79 (1997), 4453). Single-wall carbon nanotubes, on the other hand, possess properties that are significantly superior to those of multi-wall nanotubes. However, single-wall carbon nanotubes are available only in small quantities since known methods of production do not produce more than few g/day of these nanotubes. For any industrial application such as storage or material reinforcement, the amount of single-wall carbon nanotubes produced must be at least a few kilograms per day.

Nowadays, the most popular methods for producing single-wall carbon nanotubes are laser ablation, electric arc and chemical vapor deposition (CVD). The two first methods are based on the same principal: local evaporation of a graphite target enriched with a metal catalyst and subsequent condensation of the vapor to form nanotubes (A.A. Puretzky, D.B. Geohegan, S.J. Pennycook, Appl. Phys. A 70 (2000), 153). US patent No. 6,183,714 discloses a method of making ropes of single-wall carbon nanotubes using laser pulsing of a vapor

containing carbon and one or more Group VIII transition metals. US patent No. 5,424,054 discloses a process for producing hollow carbon fibers having wall consisting essentially of a single layer of carbon atoms using an electric arc. The process involves contacting carbon vapor with cobalt vapor under specific conditions, and is thus limited to the use of cobalt vapor.

Although the above methods are relatively efficient for the transformation of carbon into nanotubes, they have inherent drawbacks. The vaporisation of graphite is not energetically advantageous since 717 kJ are required to evaporate one mole of carbon. Therefore, the production of single-wall carbon nanotubes via laser ablation and electric arc consume a lot of energy for small quantities of nanotubes produced. Moreover, these processes are non-continuous since they must be stopped for renewing the source of carbon once the graphite has been consumed.

In the CVD method as well as in the other two methods described above, the metal catalyst plays a key role in the synthesis of the nanotubes. For example, in the CVD method, the carbon-containing gas is decomposed by the particles of metal catalyst on which the nanotubes form. The CVD method suffers from a major drawback since the encapsulation of the catalyst particles by carbon stops the growth of the nanotubes (R.E. Smalley et al. Chem. Phys. Lett. 296 (1998), 195). In addition, due to the non-selectivity of the method, nanotubes having two, three or multi-walls are obtained at the same time as the single-wall nanotubes.

A promising method for the production of single-wall carbon nanotubes involves the use of a plasma torch for decomposing a mixture of carbon-containing substance and a metal catalyst and then condensing the mixture to obtain single-wall carbon nanotubes. This method has been recently described by O. Smiljanic, B.L. Stansfield, J.-P. Dodelet, A. Serventi, S. Désilets, in

Chem. Phys. Lett. 356 (2002), 189 and showed encouraging results. Such a method, however, has an important drawback since a premature extinction of the plasma torch occurs due to a rapid formation of carbon deposit in the torch. This method is therefore non-continuous and requires removal of the carbon deposit. Thus, large quantities of single-wall carbon nanotubes cannot be produced.

It is therefore an object of the present invention to overcome the above drawbacks and to provide a method and apparatus for the continuous production of single-wall carbon nanotubes in large quantities.

According to a first aspect of the invention, there is provided a method for producing single-wall carbon nanotubes, comprising the steps of:

a) providing a plasma torch having a plasma tube with a plasma-discharging end;

b) feeding an inert gas through the plasma tube to form a primary plasma;

c) contacting a carbon-containing substance and a metal catalyst with the primary plasma at the plasma-discharging end of the plasma tube, to form a secondary plasma containing atoms or molecules of carbon and atoms of metal catalyst; and

d) condensing the atoms or molecules of carbon and the atoms of metal catalyst to form single-wall carbon nanotubes.

According to a second aspect of the invention, there is provided a method for producing single-wall carbon nanotubes, comprising the steps of:

a) providing a plasma torch having a plasma tube with a plasma-discharging end;

b) feeding an inert gas and an inorganic metal catalyst through the plasma tube to form a primary plasma containing the atoms of metal catalyst;

c) contacting a carbon-containing substance with the primary plasma at the plasma-discharging end of said plasma tube, to form a secondary plasma containing atoms or molecules of carbon and the atoms of metal catalyst; and

d) condensing the atoms or molecules of carbon and the atoms of metal catalyst to form single-wall carbon nanotubes.

Applicant has found quite surprisingly that by feeding the carbon-containing substance separately from the inert gas used to generate the primary plasma so that the carbon-containing substance contacts the primary plasma at the plasma-discharging end of the plasma tube to form the aforesaid secondary plasma, there is no undesirable formation of carbon deposit adjacent the plasma-discharging end of the plasma tube. Thus, no premature extinction of the plasma torch.

In the method according to the first aspect of the invention, step (c) can be carried out by separately directing the carbon-containing substance and the metal catalyst towards the primary plasma. Preferably, the carbon-containing substance is in liquid or gaseous phase and the carbon-containing substance in liquid or gaseous phase flows along a helical path prior to contacting the primary plasma. More preferably, the carbon-containing substance in liquid or gaseous phase is in admixture with a carrier gas. It is also possible to use a carbon-containing substance in solid phase, in admixture with a carrier gas, and cause the mixture to flow along a helical path prior to contacting the primary plasma. When use is made of a metal catalyst in liquid or gaseous phase, such a metal catalyst preferably flows along a helical path prior to contacting the primary plasma. The metal catalyst in liquid or gaseous phase can be in admixture with a carrier gas. It is also possible to use a metal catalyst in solid phase, in admixture with a carrier gas, and cause the mixture to flow along a helical path prior to contacting the primary plasma.

Step (c) of the method according to the first aspect of the invention can also be carried out by directing a mixture of the carbon-containing substance and the metal catalyst towards the primary plasma. Preferably, the carbon-containing substance and the metal catalyst are in liquid or gaseous phase and the latter two flow along a helical path prior to contacting the primary plasma. More preferably, the carbon-containing substance and the metal catalyst in liquid or gaseous phase are in admixture with a carrier gas. It is also possible to use the carbon-containing substance and the metal catalyst in solid phase, in admixture with a carrier gas, and cause the mixture to flow along a helical path prior to contacting the primary plasma.

The metal catalyst used in the method according to the first aspect of the invention is preferably an organometallic complex. Examples of suitable organometallic complex include those comprising at least one metal selected from the group consisting of Mo, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Y, La, Hf, V and Ta; the metal of the organometallic complex is preferably iron. It is also possible to use an inorganic metal catalyst consisting of an inorganic metal complex or of at least one metal in metallic form. Preferably, the inorganic metal complex comprises at least one metal selected from the group consisting of Mo, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Y, La, Hf, V and Ta, and the metal in metallic form is selected from the same group. More preferably, the metal in metallic form is iron.

In the method according to the first aspect of the invention, it is possible to use the inert gas in admixture with an inorganic metal catalyst which may be the same or different than the one used in step (c).

In the method according to the second aspect of the invention, step (c) can be carried out by directing the carbon-containing substance towards the primary plasma. Preferably, the carbon-containing substance is in liquid or

gaseous phase and the carbon-containing substance in liquid or gaseous phase flows along a helical path prior to contacting the primary plasma. More preferably, the carbon-containing substance in liquid or gaseous phase is in admixture with a carrier gas. It is also possible, to use a carbon-containing substance in solid phase, in admixture with a carrier gas, and cause the mixture to flow along a helical path prior to contacting the primary plasma.

The inorganic metal catalyst used in the method according to the second aspect of the invention can be an inorganic metal complex or at least one metal in metallic form. Preferably, the inorganic metal complex comprises at least one metal selected from the group consisting of Mo, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Y, La, Hf, V and Ta, and the metal in metallic form is selected from the same group. More preferably, the metal in metallic form is iron.

The carbon-containing substance used in the method according to the first or the second aspect of the invention can be a carbon-containing gas, a carbon-containing liquid or a carbon-containing solid. It is also possible to use a mixture of a carbon-containing gas and a carbon-containing liquid, a mixture of a carbon-containing gas and a carbon-containing solid, a mixture of a carbon-containing liquid and a carbon-containing solid or a mixture of a carbon-containing gas, a carbon-containing liquid and a carbon-containing solid. Preferably, the carbon-containing gas is a C_1-C_4 hydrocarbon such as methane, ethane, ethylene, acetylene, propane, propene, cyclopropane, allene, propyne, butane, 2-methylpropane, 1-butene, 2-butene, 2-methylpropene, cyclobutane, methylcyclopropane, 1-butyne, 2-butyne, cyclobutene, 1,2-butadiene, 1,3-butadiene or 1-buten-3-yne or a mixture thereof. The carbon-containing liquid is preferably a C_5-C_{17} hydrocarbon such as pentane, hexane, cyclohexane, heptane, benzene, toluene, xylene or styrene or a mixture thereof. The carbon-containing solid can be graphite, carbon black, norbornylene,

naphthalene, anthracene, phenanthrene, polyethylene, polypropylene, or polystyrene or a mixture thereof. Graphite is preferred.

The inert gas used in the method according to the first or second aspect of the invention can be helium, neon, argon, krypton, xenon or radon or a mixture thereof. Argon is preferred. A cooling inert gas is preferably injected downstream of the secondary plasma; the cooling inert gas can be helium, neon, argon, krypton, xenon or radon or a mixture thereof. The aforementioned carrier gas can be helium, neon, argon, krypton, xenon, radon, hydrogen or hydrogen sulfide or a mixture thereof. Argon is preferably used as carrier gas.

According to a preferred embodiment, the metal catalyst and the carbon-containing substance are used in a molar ratio between 0.01 and 0.06, and more preferably in a molar ratio of about 0.02.

Step (d) of the method according to the first or second aspect of the invention is preferably carried out to provide a temperature gradient permitting gradual condensation of the atoms or molecules of carbon and the atoms of metal catalyst. Preferably, the temperature gradient is provided by directing the atoms or molecules of carbon and the atoms of metal catalyst through an oven disposed downstream of the plasma tube in spaced relation thereto, the oven being heated at a predetermined temperature. The predetermined temperature is preferably comprised between 500 and 1800 °C, a temperature of about 900 °C is preferred.

The present invention also provides, in a third aspect thereof, an apparatus for carrying out a method according to the aforementioned first aspect. Such an apparatus comprises a plasma torch having a plasma tube for receiving an inert gas so as to form a primary plasma, the plasma tube having a plasma-discharging end and feed means for directing a carbon-containing

substance and a metal catalyst towards the primary plasma so that the carbon-containing substance and the metal catalyst contact the primary plasma at the plasma-discharging end of the plasma tube, to thereby form a secondary plasma containing atoms or molecules of carbon and the atoms of metal catalyst. The apparatus further includes condensing means for condensing the atoms or molecules of carbon and the atoms of metal catalyst to form single-wall carbon nanotubes.

The present invention further provides, in a fourth aspect thereof, an apparatus for carrying out a method according to the aforementioned second aspect. Such an apparatus comprises a plasma torch having a plasma tube for receiving an inert gas and an inorganic metal catalyst so as to form a primary plasma containing atoms of metal catalyst, the plasma tube having a plasma-discharging end and feed means for directing a carbon-containing substance towards the primary plasma so that the carbon-containing substance contacts the primary plasma at the plasma-discharging end of the plasma tube, to thereby form a secondary plasma containing atoms or molecules of carbon and the atoms of metal catalyst. The apparatus also includes condensing means for condensing the atoms or molecules of carbon and the atoms of metal catalyst to form single-wall carbon nanotubes.

In the apparatus according to the third aspect of the invention, the feed means preferably comprise a first conduit for directing the carbon-containing substance towards the primary plasma and a second conduit for directing the metal catalyst towards the primary plasma. Preferably, the first and second conduits each have a discharge end disposed adjacent the plasma-discharging end of the plasma tube. Alternatively, the feed means can comprise a single conduit for directing a mixture of the carbon-containing substance and the metal catalyst towards the primary plasma. In such a case, the single conduit preferably has a discharge end disposed adjacent the plasma-discharging end of

the plasma tube. In a particularly preferred embodiment, the single conduit is disposed inside the plasma tube and extends coaxially thereof.

In the apparatus according to the fourth aspect of the invention, the feed means preferably comprises a single conduit for directing the carbon-containing substance towards the primary plasma. Preferably, the conduit has a discharge end disposed adjacent the plasma-discharging end of the plasma tube. In a particularly preferred embodiment, the conduit is disposed inside the plasma tube and extends coaxially thereof.

In the apparatus according to the third or fourth aspect of the invention, the condensing means preferably comprise an oven disposed downstream of the plasma tube in spaced relation thereto, and a heat source for heating the oven to provide a temperature gradient permitting gradual condensation of the atoms or molecules of carbon and the atoms of metal catalyst. Preferably, a heat-resistant tubular member having a plasma-receiving end extends through the oven with the plasma-receiving end disposed upstream of the plasma-discharging end of the plasma tube. Injection means are provided for injecting a cooling inert gas into the tubular member, downstream of the secondary plasma; the cooling inert gas assists in providing the temperature gradient. The heat-resistant tubular member can be made of quartz or boron nitride.

Where the apparatus according to the third or fourth aspect of the invention has the aforementioned conduit disposed inside the plasma tube and extending coaxially thereof, the apparatus preferably includes a further heat-resistant tubular member disposed about the plasma tube and extending coaxially thereof, and means for injecting a further inert gas between the plasma tube and the tubular member to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end of the plasma tube.

Further features and advantages of the invention will become more readily apparent from the following description of preferred embodiments as illustrated by way of examples in the appended drawings wherein:

Figure 1 is a schematic, sectional elevation view of an apparatus for producing single-wall carbon nanotubes, according to a first preferred embodiment of the invention;

Figure 2 is a schematic, sectional elevation view of an apparatus for producing single-wall carbon nanotubes, according to a second preferred embodiment of the invention; and

Figure 3 is a schematic, sectional elevation view of an apparatus for producing single-wall carbon nanotubes, according to a third preferred embodiment of the invention.

Referring first to Figure 1, there is shown an apparatus 10 for producing single-wall carbon nanotubes, which comprises a plasma torch 12 having a plasma tube 14 with a plasma-discharging end 16, and an oven 18 disposed downstream of the plasma tube 14 in spaced relation thereto. The plasma tube 14 is adapted to receive an inert gas for activation by electromagnetic radiation generated from a source (not shown) so as to form a primary plasma 20. A feed conduit 22 having a discharge end 24 is arranged inside the plasma tube 14 and extends coaxially thereof. The discharge end 24 of the feed conduit 22 is disposed adjacent the plasma discharging end 16 of the plasma tube 14. The feed conduit 22 serves to direct a carbon-containing substance, such as a carbon-containing gas, and a metal catalyst towards the primary plasma 20 so that the carbon-containing substance and the metal catalyst contact the primary plasma 20 at the plasma-discharging end 16 of the plasma tube 14, whereby to form a secondary plasma 26 containing atoms or molecules of carbon and the

atoms of metal catalyst. The carbon-containing gas is preferably ethylene or methane.

The oven 18 serves to condense the atoms or molecules of carbon and atoms of metal catalyst to form single-wall carbon nanotubes 28. A heat source 30 is provided for heating the oven 18 to generate a temperature gradient permitting gradual condensation of the atoms or molecules of carbon and the atoms of metal catalyst. A heat-resistant tubular member 32 having a plasma-receiving end 34 extends through the oven 18, the plasma-receiving end 34 being disposed upstream of the plasma-discharging end 16 of the plasma tube 14. The apparatus further includes a gas injector 36 for injecting a cooling inert gas into the tubular member 32, downstream of the secondary plasma 26. The cooling inert gas assists in providing the temperature gradient. Another heat-resistant tubular member 38 is disposed about the plasma tube 14 and extends coaxially thereof, the tubular member 38 being fixed to the tubular member 32 and supporting same. Another gas injector 42 is provided for injecting a further inert gas between the plasma tube 14 and the tubular member 38 to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end 16 of said plasma tube 14.

The inert gas flows through the plasma tube 14 along a helical path represented by the arrow 44. Similarly, the carbon-containing gas and the metal catalyst, optionally in admixture with a carrier gas, flow through the feed conduit 22 along a helical path represented by the arrow 46. The metal catalyst which is fed through the conduit 22 can be either an organometallic complex such as ferrocene, or an inorganic metal catalyst such as iron. Instead of feeding the metal catalyst through the conduit 22, it is possible to feed only the carbon-containing gas through the conduit 22 and to feed the metal catalyst in admixture with the inert gas through the plasma tube 14. In such a case, the metal catalyst must be an inorganic metal catalyst to prevent undesirable

formation of carbon deposit adjacent the plasma-discharging end 16 of the plasma tube 14. It is also possible to feed the inert gas and an inorganic metal catalyst through the plasma tube 14 and to feed the carbon-containing gas in admixture with an organometallic complex or an inorganic metal catalyst through the conduit 22.

Figure 2 illustrates another apparatus 48 for producing single-wall carbon nanotubes, which comprises a plasma torch 50 having a plasma tube 52 with a plasma-discharging end 54, and an oven 56 disposed downstream of the plasma tube 52 in spaced relation thereto. The plasma tube 52 is adapted to receive an inert gas for activation by electromagnetic radiation generated from a source (not shown) so as to form a primary plasma 58. A feed conduit 60 having a discharge end 62 disposed adjacent the plasma-discharging end 54 of the plasma tube 52 is provided for directing a carbon-containing substance, such as a carbon-containing gas, and a metal catalyst towards the primary plasma 58. The carbon-containing substance and the metal catalyst discharged from the feed conduit 60 contact the primary plasma 58 at the plasma-discharging end 54 of the plasma tube 52, thereby forming a secondary plasma 64 containing atoms or molecules of carbon and the atoms of metal catalyst. The carbon-containing gas is preferably ethylene or methane. Although only one feed conduit 60 is shown in Figure 2, it is possible to have a plurality of such conduits disposed symmetrically about the plasma tube 52.

The oven 56 serves to condense the atoms or molecules of carbon and the atoms of metal catalyst to form single-wall carbon nanotubes 66. A heat source 68 is provided for heating the oven 56 to generate a temperature gradient permitting gradual condensation of the atoms or molecules of carbon and the atoms of metal catalyst. A heat-resistant tubular member 70 having a plasma-receiving end 72 extends through the oven 56, the plasma-receiving end 72 being disposed upstream of the plasma-discharging end 54 of the

plasma tube 52. The apparatus further includes a gas injector 74 for injecting a cooling inert gas into the tubular member 70, downstream of the secondary plasma 64. The cooling inert gas assists in providing the temperature gradient.

The inert gas flows through the plasma tube 52 along a helical path represented by the arrow 76. Similarly, the carbon-containing gas and the metal catalyst, optionally in admixture with a carrier gas, flow through the conduit 60 along a helical path represented by the arrow 78. The metal catalyst which is fed through the conduit 60 can be either an organometallic complex such as ferrocene, or an inorganic metal catalyst such as iron. Instead of feeding the metal catalyst through the conduit 60, it is possible to feed only the carbon-containing gas through the conduit 60 and to feed the metal catalyst in admixture with the inert gas through the plasma tube 52. In such a case, the metal catalyst must be an inorganic metal catalyst to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end 54 of the plasma tube 52. It is also possible to feed the inert gas and an inorganic metal catalyst through the plasma tube 52 and to feed the carbon-containing gas in admixture with an organometallic complex or an inorganic metal catalyst through the conduit 60.

The apparatus 48' illustrated in Figure 3 is similar to the apparatus 48 shown in Figure 2, with the exception that an additional feed conduit 60' is provided, the feed conduits 60 and 60' being arranged on either side of the plasma tube 52. The conduit 60' has a discharge end 62' disposed adjacent the plasma-discharging end 54 of the plasma tube 52 and serves the same purpose as the feed conduit 60. The carbon-containing gas and the metal catalyst, optionally in admixture with a carrier gas, flow through the conduit 60' along a helical path represented by the arrow 78'. Although two feed conduits 60 and 60' are shown in Figure 3, it is possible to have a plurality of such conduits disposed symmetrically about the plasma tube 52. Instead of feeding the metal

catalyst through the conduits 60 and 60', it is possible to feed only the carbon-containing gas through the conduits 60 and 60' and to feed the metal catalyst in admixture with the inert gas through the plasma tube 52. In such a case, the metal catalyst must be an inorganic metal catalyst to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end 54 of the plasma tube 52. It is also possible to feed the inert gas and an inorganic metal catalyst through the plasma tube 52 and to feed the carbon-containing gas in admixture with an organometallic complex or an inorganic metal catalyst through the conduits 60 and 60'.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for producing single-wall carbon nanotubes, comprising the steps of:

a) providing a plasma torch having a plasma tube with a plasma-discharging end;

b) feeding an inert gas through said plasma tube to form a primary plasma;

c) contacting a carbon-containing substance and a metal catalyst with said primary plasma at the plasma-discharging end of said plasma tube, to form a secondary plasma containing atoms or molecules of carbon and atoms of said metal catalyst; and

d) condensing the atoms or molecules of carbon and the atoms of said metal catalyst to form single-wall carbon nanotubes.

2. The method of claim 1, wherein step (c) is carried out by separately directing the carbon-containing substance and the metal catalyst towards the primary plasma.

3. The method of claim 2, wherein the carbon-containing substance is in liquid or gaseous phase and the carbon-containing substance in liquid or gaseous phase flows along a helical path prior to contacting the primary plasma.

4. The method of claim 2 or 3, wherein the carbon-containing substance is in gaseous phase and the carbon-containing substance in gaseous phase is in admixture with a carrier gas.

5. The method of claim 2 or 3, wherein the carbon-containing substance is in liquid phase and the carbon-containing substance in liquid phase is in admixture with a carrier gas.

6. The method of claim 2, wherein the carbon-containing substance is in solid phase and the carbon-containing substance in solid phase is in admixture with a carrier gas, and wherein the mixture of the carbon-containing substance in solid phase and the carrier gas flows along a helical path prior to contacting the primary plasma.

7. The method of any one of claim 2 to 6, wherein the metal catalyst is in liquid or gaseous phase and the metal catalyst in liquid or gaseous phase flows along a helical path prior to contacting the primary plasma.

8. The method of claim 2 or 7, wherein the metal catalyst is in gaseous phase and the metal catalyst in gaseous phase is in admixture with a carrier gas.

9. The method of claim 2 or 7, wherein the metal catalyst is in liquid phase and the metal catalyst in liquid phase is in admixture with a carrier gas.

10. The method of claim 2, wherein the metal catalyst is in solid phase and the metal catalyst in solid phase is in admixture with a carrier gas, and wherein the mixture of the metal catalyst in solid phase and the carrier gas flows along a helical path prior to contacting the primary plasma.

11. The method of claim 1, wherein step (c) is carried out by directing a mixture of the carbon-containing substance and the metal catalyst towards the primary plasma.

12. The method of claim 11, wherein the carbon-containing substance and the metal catalyst are in liquid or gaseous phase and the carbon-containing substance and metal catalyst in liquid or gaseous phase flow along a helical path prior to contacting the primary plasma.

13. The method of claim 11 or 12, wherein the carbon-containing substance and the metal catalyst are in gaseous phase and the carbon-containing substance and metal catalyst in gaseous phase are in admixture with a carrier gas.

14. The method of claim 11 or 12, wherein the carbon-containing substance and the metal catalyst are in liquid phase and the carbon-containing substance and metal catalyst in liquid phase are in admixture with a carrier gas.

15. The method of claim 11, wherein the carbon-containing substance and the metal catalyst are in solid phase and the carbon-containing substance and metal catalyst in solid phase are in admixture with a carrier gas, and wherein the mixture of the carbon-containing substance, the metal catalyst in solid phase and the carrier gas flows along a helical path prior to contacting the primary plasma.

16. The method of any one of claims 1 to 15, wherein the metal catalyst is an organometallic complex.

17. The method of claim 16, wherein the organometallic complex comprises at least one metal selected from the group consisting of Mo, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Y, La, Hf, V and Ta.

18. The method of claim 17, wherein the metal of the organometallic complex is iron.

19. The method of claim 18, wherein the organometallic complex is ferrocene.

20. The method of any one of claims 1 to 15, wherein the metal catalyst is an inorganic metal catalyst.

21. The method of any one of claims 1 to 15, wherein the inert gas is in admixture with an inorganic metal catalyst.

22. A method for producing single-wall carbon nanotubes, comprising the steps of:

a) providing a plasma torch having a plasma tube with a plasma-discharging end;
b) feeding an inert gas and an inorganic metal catalyst through said plasma tube to form a primary plasma containing atoms of said metal catalyst;
c) contacting a carbon-containing substance with said primary plasma at the plasma-discharging end of said plasma tube, to form a secondary plasma containing atoms or molecules of carbon and the atoms of said metal catalyst; and
d) condensing the atoms or molecules of carbon and the atoms of said metal catalyst to form single-wall carbon nanotubes.

23. The method of claim 22, wherein step (c) is carried out by directing the carbon-containing substance towards the primary plasma.

24. The method of claim 23, wherein the carbon-containing substance is in liquid or gaseous phase and the carbon-containing substance in liquid or gaseous phase flows along a helical path prior to contacting the primary plasma.

25. The method of claim 23 or 24, wherein the carbon-containing substance is in gaseous phase and the carbon-containing substance in gaseous phase is in admixture with a carrier gas.

26. The method of claim 23 or 24, wherein the carbon-containing substance is in liquid phase and the carbon-containing substance in liquid phase is in admixture with a carrier gas.

27. The method of claim 23, wherein the carbon-containing substance is in solid phase and the carbon-containing substance in solid phase is in admixture with a carrier gas, and wherein the mixture of the carbon-containing substance in solid phase and the carrier gas flows along a helical path prior to contacting the primary plasma.

28. The method of any one of claims 20 to 27, wherein the inorganic metal catalyst is an inorganic metal complex.

29. The method of claim 28, wherein the inorganic metal complex comprises at least one metal selected from the group consisting of Mo, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Y, La, Hf, V and Ta.

30. The method of any one of claims 20 to 27, wherein the inorganic metal catalyst comprises at least one metal in metallic form.

31. The method of claim 30, wherein the metal in metallic form is selected from the group consisting of Mo, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Y, La, Hf, V and Ta.

32. The method of claim 31, wherein the metal in metallic form is iron.

33. The method of any one of claims 1 to 32, wherein the carbon-containing substance is a carbon-containing gas.

34. The method of any one of claims 1 to 32, wherein the carbon-containing substance is a carbon-containing liquid.

35. The method of any one of claims 1 to 32, wherein the carbon-containing substance is a carbon-containing solid.

36. The method of any one of claims 1 to 32, wherein the carbon-containing substance comprises a mixture of a carbon-containing gas and a carbon-containing liquid.

37. The method of any one of claims 1 to 32, wherein the carbon-containing substance comprises a mixture of a carbon-containing gas and a carbon-containing solid.

38. The method of any one of claims 1 to 32, wherein the carbon-containing substance comprises a mixture of a carbon-containing liquid and a carbon-containing solid.

39. The method of any one of claims 1 to 32, wherein the carbon-containing substance comprises a mixture of a carbon-containing gas, a carbon-containing liquid and a carbon-containing solid.

40. The method of any one of claims 33, 36, 37 and 39, wherein the carbon-containing gas is a C_1-C_4 hydrocarbon.

41. The method of claim 40, wherein the hydrocarbon is selected from the group consisting of methane, ethane, ethylene, acetylene, propane, propene, cyclopropane, allene, propyne, butane, 2-methylpropane, 1-butene, 2-butene, 2-methylpropene, cyclobutane, methylcyclopropane, 1-butyne, 2-butyne, cyclobutene, 1,2-butadiene, 1,3-butadiene, 1-buten-3-yne and mixtures thereof.

42. The method of claim 41, wherein the hydrocarbon is methane or ethylene.

43. The method of any one of claims 34, 36, 38 and 39, wherein the carbon-containing liquid is a C_5-C_{17} hydrocarbon.

44. The method of claim 43, wherein the hydrocarbon is selected from the group consisting of pentane, hexane, cyclohexane, heptane, benzene, toluene, xylene, styrene, and mixtures thereof.

45. The method of any one of claims 35, 37, 38 and 39, wherein the carbon-containing solid is selected from the group consisting of graphite, carbon black, norbornylene, naphthalene, anthracene, phenanthrene, polyethylene, polypropylene, polystyrene and mixtures thereof.

46. The method of claim 45, wherein the carbon containing solid is graphite.

47. The method of any one of claims 1 to 46, wherein the inert gas is selected from the group consisting of helium, neon, argon, krypton, xenon, radon and mixtures thereof.

48. The method of claim 47, wherein the inert gas is argon.

49. The method of any one of claims 1 to 48, wherein the inert gas flows along a helical path.

50. The method of any one of claims 1 to 49, wherein a cooling inert gas is injected downstream of the secondary plasma.

51. The method of claim 50, wherein the cooling inert gas is selected from the group consisting of helium, neon, argon, krypton, xenon, radon and mixtures thereof.

52. The method of any one of claims 4, 5, 6, 8, 9, 10, 13, 14, 15, 25, 26, and 27, wherein the carrier gas is selected from the group consisting of helium, neon, argon, krypton, xenon, radon, hydrogen, hydrogen sulfide and mixtures thereof.

53. The method of claim 52, wherein the carrier gas is argon.

54. The method of any one of claims 1 to 53, wherein the metal catalyst and the carbon-containing substance are used in a molar ratio between 0.01 and 0.06.

55. The method of claim 54, wherein the molar ratio is about 0.02.

56. The method of any one of claims 1 to 55, wherein step (d) is carried out to provide a temperature gradient permitting gradual condensation of the atoms or molecules of carbon and the atoms of said metal catalyst.

57. The method of claim 56, wherein said temperature gradient is provided by directing the atoms or molecules of carbon and the atoms of said

metal catalyst through an oven disposed downstream of said plasma tube in spaced relation thereto, said oven being heated at a predetermined temperature.

58. The method of claim 57, wherein said predetermined temperature is comprised between 500 and 1800 °C.

59. The method of claim 58, wherein said predetermined temperature is about 900 °C.

60. An apparatus for producing single-wall carbon nanotubes, which comprises:

a plasma torch having a plasma tube for receiving an inert gas so as to form a primary plasma, said plasma tube having a plasma-discharging end;

feed means for directing a carbon-containing substance and a metal catalyst towards said primary plasma so that the carbon-containing substance and the metal catalyst contact said primary plasma at the plasma-discharging end of said plasma tube, to thereby form a secondary plasma containing atoms or molecules of carbon and the atoms of said metal catalyst; and

condensing means for condensing the atoms or molecules of carbon and the atoms of said metal catalyst to form single-wall carbon nanotubes.

61. The apparatus of claim 60, wherein said feed means comprise a first conduit for directing said carbon-containing substance towards the primary plasma and a second conduit for directing said metal catalyst towards the primary plasma.

62. The apparatus of claim 61, wherein said first and second conduits each have a discharge end disposed adjacent the plasma-discharging end of said plasma tube.

63. The apparatus of claim 60, wherein said feed means comprise a single conduit for directing a mixture of the carbon-containing substance and the metal catalyst towards the primary plasma.

64. The apparatus of claim 63, wherein said conduit has a discharge end disposed adjacent the plasma-discharging end of said plasma tube.

65. The apparatus of claim 62, wherein said conduit is disposed inside said plasma tube and extends coaxially thereof.

66. An apparatus for producing single-wall carbon nanotubes, which comprises:

a plasma torch having a plasma tube for receiving an inert gas and an inorganic metal catalyst so as to form a primary plasma containing atoms of said metal catalyst, said plasma tube having a plasma-discharging end;

feed means for directing a carbon-containing substance towards said primary plasma so that the carbon-containing substance contacts said primary plasma at the plasma-discharging end of said plasma tube, to thereby form a secondary plasma containing atoms or molecules of carbon and the atoms of said metal catalyst; and

condensing means for condensing the atoms or molecules of carbon and the atoms of said metal catalyst to form single-wall carbon nanotubes.

67. The apparatus of claim 66, wherein said feed means comprise a single conduit for directing the carbon-containing substance towards the primary plasma.

68. The apparatus of claim 67, wherein said conduit has a discharge end disposed adjacent the plasma-discharging end of said plasma tube.

69. The apparatus of claim 68, wherein said conduit is disposed inside said plasma tube and extends coaxially thereof.

70. The apparatus of any one of claims 60 to 69, wherein said condensing means comprise an oven disposed downstream of said plasma tube in spaced relation thereto, and a heat source for heating said oven to provide a temperature gradient permitting gradual condensation of the atoms or molecules of carbon and the atoms of said metal catalyst.

71. The apparatus of claim 70, further including a heat-resistant tubular member extending through said oven and having a plasma-receiving end disposed upstream of the plasma-discharging end of said plasma tube, and injection means for injecting a cooling inert gas into said tubular member and downstream of the secondary plasma, said cooling inert gas assisting in providing the temperature gradient.

72. The apparatus of claim 71, wherein said heat-resistant tubular member is made of quartz or boron nitride.

73. The apparatus of claim 65 or 69, further including a heat-resistant tubular member disposed about said plasma tube and extending coaxially thereof, and means for injecting a further inert gas between said plasma tube

and said tubular member to prevent undesirable formation of carbon deposit adjacent the plasma-discharging end of said plasma tube.

ABSTRACT

The invention relates to a method for producing single-wall carbon nanotubes. The method of the invention comprises the steps of (a) providing a plasma torch having a plasma tube with a plasma-discharging end; (b) feeding an inert gas through the plasma tube to form a primary plasma; (c) contacting a carbon-containing substance and a metal catalyst with the primary plasma at the plasma-discharging end of the plasma tube, to form a secondary plasma containing atoms or molecules of carbon and atoms of the metal catalyst; and (d) condensing the atoms or molecules of carbon and the atoms of the metal catalyst to form single-wall carbon nanotubes. Alternatively, steps (b) and (c) can be carried out by feeding an inert gas and an inorganic metal catalyst through the plasma tube to form a primary plasma containing atoms of the inorganic metal catalyst and contacting a carbon-containing substance with the primary plasma at the plasma-discharging end of the plasma tube, to form a secondary plasma containing atoms or molecules of carbon and the atoms of metal catalyst. An apparatus for carrying out the method according to the invention is also disclosed.

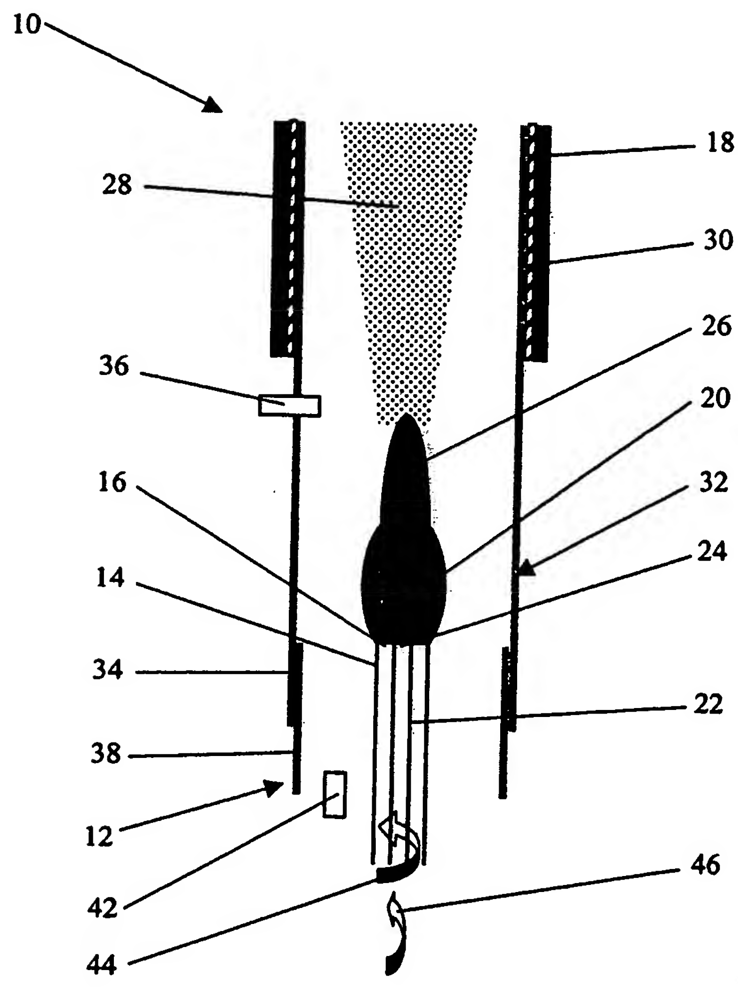

Figure 1

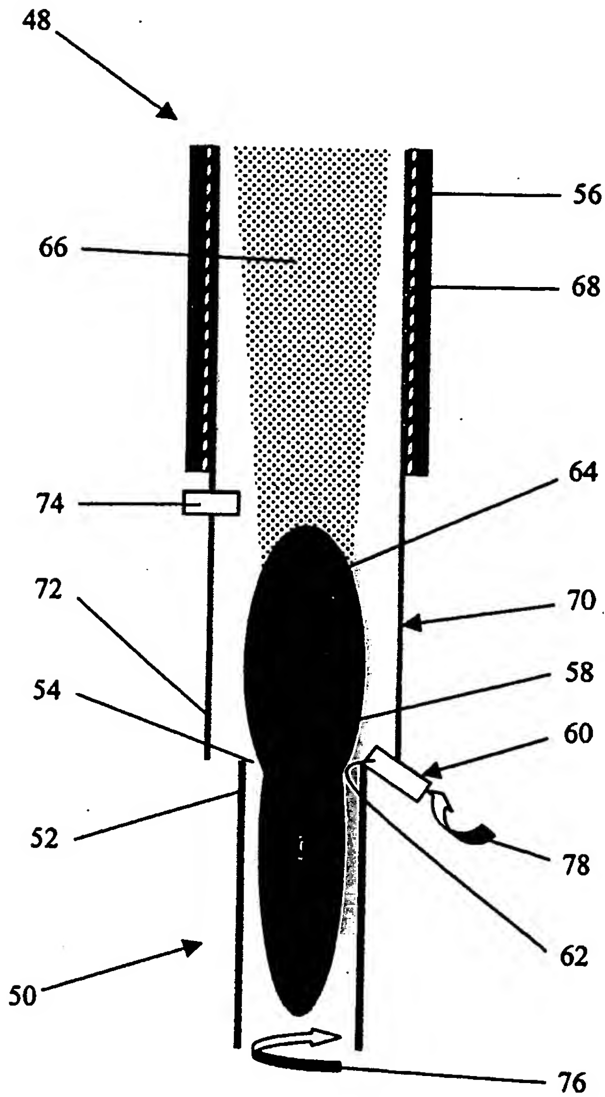

Figure 2

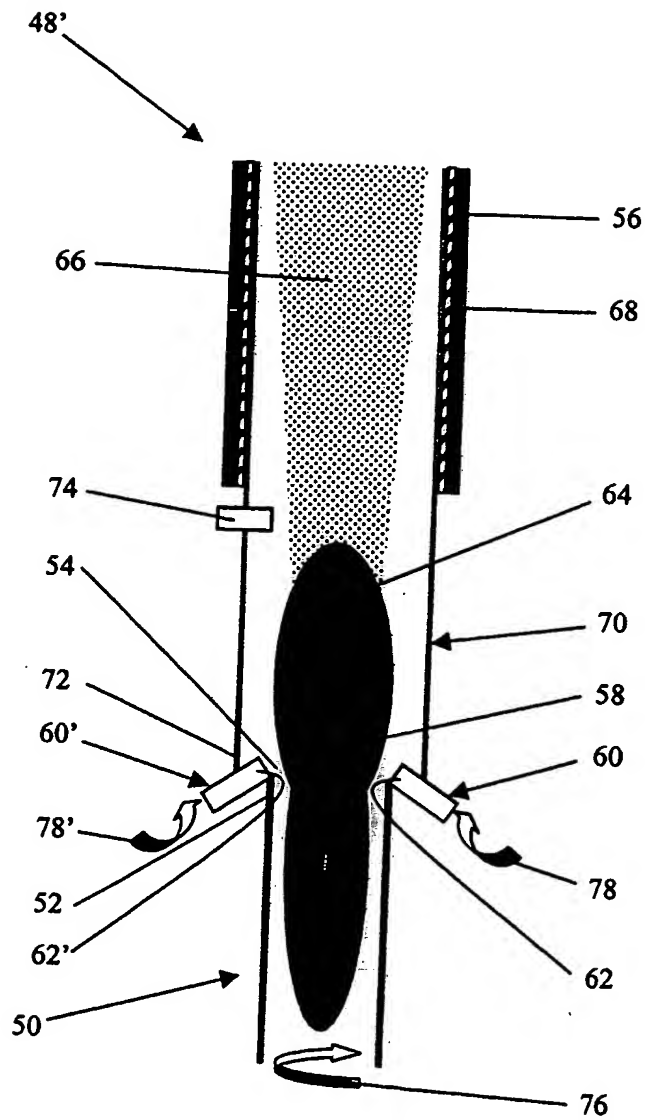

Figure 3

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